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Short-range structural transformations in water at high pressures

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ABSTRACT

We report results of molecular dynamics simulations of liquid water at the temperature $T = 277$ K for a range of high pressure. One aim of the study was to test the model Amoeba potential for the description of equilibrium structural properties and dynamical processes in liquid water. In comparing our numerical results with the Amoeba and TIP5P potentials, our results of *ab initio* molecular dynamics simulations and the experimental data reveal that the Amoeba potential reproduces correctly structural properties of the liquid water. Another aim of our work was related with the investigation of the pressure induced structural transformations and their influence on the microscopic collective dynamics. We have found that the structural anomaly at the pressure $p_c \approx 2000$ Atm is related with the changes of the local, short-range order in liquid water within the first two coordination shells. This anomaly specifies mainly by deformation of the hydrogen-bond network. We also discuss in detail the anomalous behavior of sound propagation in liquid water at high pressures and compare numerical results with the experimental data.

1. Introduction

Water is one of the most widespread liquids in wildlife and has a great number of chemical and technological applications [1]. Although a particular water molecule has a simple chemical structure, a water system is considered as a complex fluid because of its anomalous behavior in thermodynamical, structural and transport properties [2]. It dilates with solidification, and the density has a maximum at the pressure 1.0 Atm and the temperature 277 K [3]. Additionally, there is a minimum in the isothermal compressibility at 319 K and a clear minimum in the isobaric heat capacity at 308 K. These anomalies are linked with the microscopic structure of liquid water [4], which can be regarded as a *transient gel* — a highly associated liquid with strongly directional hydrogen bonds [5,6].

An active study of the different characteristics and properties of the water system is provided by the development of the numerical methods of the computer simulations. So, the first study of the water "structure" was performed by Barker and Watts within the Monte-Carlo method [7]. They have computed the energy, heat capacity and radial distribution function for water system at the temperature 298 K and have compared the obtained results with the experimental data. The considered system was very small, 64 molecules interacted via the Rowlinson potential [8]. In the next study performed by Rahman and Stillinger [9] the water system was simulated through 216 rigid molecules interacted by means of the pair-additive effective potential. The authors have investigated in detail the structural, transport and dynamic properties of liquid water at the temperature 307.3 K. The molecular dynamics simulations in the low temperature thermodynamic phase range were performed by Ref. [10]. Here, the "*second critical point*" at the temperature $T = 223$ K and pressure $p = 1000$ Atm was found. Below this second critical point, the liquid phase separates into two distinct phases — *a low-density liquid* and *a high-density liquid*. It is necessary to note that to study the water system a great number of the model potentials for intramolecular and intermolecular interactions were suggested (see, for example, review [11]). Here, the first model of the liquid water was proposed in 1933 by Bernal and Fowler [12]: an ice-like disordered tetrahedral structure arising from the electrostatic interactions between close neighbors.

The special role in the understanding of the microdynamic features of the water have the methods of *ab-initio* simulations based on the density functional theory. So, one of the first works, where the Car–Parrinello method was applied to study dynamic properties in water, was done by Laasonen et al. [13]. They also found that the local density approximation gives realistic results for the intramolecular properties without gradient corrections, but it fails to give a correct description of the intermolecular interactions and the binding properties. Later, the numerous *ab-initio* simulations for water system have been done [14–18].

Recently, a large amount of the works were intended for the investigation of water structural, transport, mechanical properties at the different externally applied conditions [19–23]. For example, the processes of the dissociation of the water molecules at the pressures 14.5 GPa and 26.8 GPa were investigated in Ref. [24] by means of *ab-initio* molecular dynamics simulations. Molecular dynamics simulations of water at the negative pressures were carried out with two model potentials of interparticle interaction: the extended simple point charge (SPC/E) and the Mahoney–Jorgensen transferable intermolecular potential with five points (TIP5P). The equilibrium phase diagram

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